NAVAL FACILITIES ENGINEERING SERVICE CENTER
Port Hueneme, CA 93043

NFESC
TECHNICAL REPORT
TR-2107-ENV

EVALUATION OF BIO-BASED INDUSTRIAL PRODUCTS FOR NAVY AND DOD USE

PHASE I

CITRA-SOLV®
NATURAL CITRUS CLEANER & DEGREASER

April 1999

Prepared by
Naval Facilities Engineering Service Center
1100 23rd Avenue
Port Hueneme, CA 93043-4370

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1.0 INTRODUCTION

Alternative Agricultural Research and Commercialization (AARC) Corporation is a wholly owned corporation of the U.S. Department of Agriculture (USDA). AARC is a venture capital firm that is authorized to make investments in companies to help commercialize bio-based industrial products (non-food, non-feed) from agricultural, forestry materials, and animal byproducts. As these bio-based products are made from agricultural materials, they tend to be environmentally friendly. In many instances, these products replace petroleum products or are comprised of recovered agricultural waste material.

Since the Federal government has an equity position in these companies, Section 729 of the 1996 Federal Agricultural Improvement and Reform Act (P.L.104-127, Title VII, Subtitle A, Chapter 2, Section 1657c) prompted an amendment of the AARC Corporation authorization. The authorization now allows other Federal agencies to establish procurement set-asides and encourages preferences for property that has been commercialized with assistance provided under Subtitle G of Title XVI of the Food, Agriculture, Conservation and Trade Act of 1990. To this end, the Federal Acquisition Regulations are in the process of being amended to encourage these preferences. In addition, both the Secretary of Defense and the Secretary of Agriculture have signed letters expressing their support of a partnership between Department of Defense (DoD) and USDA to increase DoD use of these bio-based products.

Under the sponsorship of AARC Corporation, Naval Facilities Engineering Service Center (NFESC) evaluated the potential use of a number of these bio-based products within the Navy and DoD. Representatives from both NFESC and AARC selected eleven bio-based products to undergo a two-phase evaluation process. This document provides the results from the first phase of the evaluation process.

2.0 EVALUATION METHODOLOGY

The evaluation methodology consists of a two-phase approach. Details of the methodology are outlined in the following two subsections.

2.1 Phase I: Preliminary Product Evaluation

Each vendor's manufacturing site was visited to collect product data, discuss product usage, and to obtain information regarding the performance claims, savings, and environmental benefits. Existing third-party certifications and test results were also reviewed and current users of the product were contacted and interviewed. In addition, scientific and engineering literature was researched to establish the physical, chemical, or biological mechanisms employed by the product in achieving its claimed performance. Potential opportunities for using the product within the Navy were identified and a preliminary life cycle cost (LCC) analysis was performed using the Phase I product data. The evaluation process will not proceed to Phase II if the results of the Phase I product investigation clearly indicates that the product can not be cost-effectively employed within the Navy or that the product has no apparent cost-effective potential for Navy

use. An implementation plan will be developed for those Phase I products evaluated as having cost effective use within the Navy. Proceeding onward to Phase II product testing will be recommended when the Phase I analysis suggests that the product has potential for cost-effective Navy use but lacks sufficient data to conclusively validate product performance and/or LCC.

2.2 Phase II: Product Testing

For those products proceeding onto phase II of the evaluation process, a specific step-by-step test protocol will be developed for each recommended product with the objective of providing sufficient data to verify product utility within the Navy. The protocol will be designed to evaluate life cycle performance of the product. Upon approval of the protocol by AARC, the product will be tested by a certified testing facility under controlled conditions. In addition, the life cycle performance of the product will be evaluated and the environmental, safety, and health benefits and trade-offs associated with the product will be estimated. A LCC analysis of the product will be performed using the proven costing techniques from the NAVFAC Economic Analysis Handbook P-442.

An implementation plan will be developed for each of the recommended products targeted for the potential user community within the Navy and DoD. During the development of the implementation plan, the requirements and needs of the Navy ship, aviation, and shore facilities will be considered. The resources of the Joint Group on Acquisition Pollution Prevention (JG-APP) will also be utilized to promote Army and Air Force implementation of the product. Product visibility may also be achieved through various publications distributed throughout DoD and other government agencies.

3.0 PRODUCTS EVALUATED

Table 3.1 lists the eleven products evaluated in Phase I for potential application within the DoD. Each product evaluation is presented in a separate report.

(Table 3.1 Omitted Due To Restricted Vendor Information)

4.0 AFFIRMATIVE PROCUREMENT

Section 6002 of Resource Conservation Recovery Act (RCRA) directs government agencies to promote recycling by increasing their purchases of products containing recovered materials. RCRA section 6002(e) requires the Environmental Protection Agency (EPA) to designate items that are or can be produced with recovered materials and prepare guidelines to assist procuring agencies in complying with their affirmative procurement responsibilities set forth in paragraphs (c), (d), and (i) of section 6002. Once EPA has designated items, section 6002 requires that any procuring agency spending more than $10,000 a year of Federal funds on an item must purchase the highest percentage of recovered materials practicable. Procuring agencies are Federal, state, and local agencies, and their contractors, which use appropriated Federal funds.

Executive Order 12873 reinforced RCRA's Federal buy recycled program by directing EPA to adopt modified procedures for designating items and providing procurement recommendations. Under the order, EPA issued a regulation known as Comprehensive Procurement Guideline which contains the item designations, and also prepared a guidance document known as a Recovered Materials Advisory Notice (RMAN). The RMAN contains EPA's recommendations to procuring agencies to assist them in purchasing the designated items and meeting their statutory obligations. The RMAN also provides general guidance for developing an affirmative procurement program. An affirmative procurement program is a procuring agency's strategy for maximizing its purchases of EPA-designated items, and must consist of the following:

- Recovered materials preference program
- An agency promotion program
- A program for requiring vendors to reasonably estimate, certify, and verify the recovered materials content of their products; and
- A program to monitor and annually review the effectiveness of the affirmative procurement program

On September 16, 1998 Executive Order 12873 was replaced by Executive Order 13101 which expanded the affirmative procurement program to include bio-based products on the EPA designated item list. A bio-based product list will be developed and published by USDA in the Federal Register no later than March 23, 1999. The list shall also be updated biannually after publication to include additional items. It is assumed that the bio-based products evaluated in this report will be included in the list.

In the spirit of section 6002 of RCRA and Executive Order 13101, Federal procuring agencies and personnel should strongly consider implementing sustainable bio-based products when selecting items to meet the goals of the affirmative procurement program.

5.0 CITRA-SOLV® NATURAL CITRUS CLEANER & DEGREASER

5.1 Product Description

Citra-Solv® Natural Citrus Cleaner & Degreaser is a revolutionary, all-purpose, household, automotive, and industrial solvent/cleaner. This product is marketed by Shadow Lake®, Inc., formerly Chempoint Products, Inc., and has been in production for nearly 10 years. Citra-Solv® was developed to replace mutagenic and carcinogenic solvents in the workplace in response to Occupational Safety and Health Administration (OSHA) regulations. Citra-Solv® is a concentrated d-limonene based product derived from the extract of citrus peels. The product contains 80-95 wt% limonene fraction terpenes, 1-10 wt% folded orange oil (the concentrated product obtained by high vacuum distillation of winterized oils of fresh oranges), 1-10 wt% ethoxylated alcohols C9-C11 and 1-10 wt% coconut diethanolamide.

Citra-Solv® is a powerful, concentrated cleaner. When diluted with water, it yields gallons of multipurpose cleaner. Not only is Citra-Solv® tough on grease and grime, but its active ingredient is made from a by-product of the orange juice industry and is a completely renewable resource. The orange scent makes it pleasant to use and its efficacy and environmental soundness have been recognized by Green Seal, Inc., an independent, nonprofit organization dedicated to protecting the environment by promoting the manufacture and sale of environmentally responsible consumer products. Additional information on Green Seal's environmental standards and recommended general-purpose cleaners, can be found on the following Websites:

http://www.greenseal.org/index.htm (Green Seal, Inc., Home Page)

http://www.greenseal.org/chart.htm (Recommended General-purpose Cleaners)

http://www.greenseal.org/standard/h-cleanr.htm (Household Cleaner Standard)

Citra-Solv® is packaged in a variety of sizes ranging from a 2-ounce promotional size to 55-gallon drums and is available in a ready-to-use spray formula. The pre-mixed product provides the natural cleaning ingredients of the super concentrated formula, but in a dilution that makes it perfect for most general household and shop uses. Citra-Solv® is available through General Services Administration (GSA) under contract number GS07F-0113H. Citra-Solv® is also available through a growing number of retailers and mail order suppliers. Appendix A includes a GSA net price listing of Citra-Solv®. Tables 5.1 and 5.2 contain a list of key retailers/distributors and mail order suppliers of Citra-Solv®.

Table 5.1 Key Retailers/Distributors of Citra-Solv® Natural Citrus Cleaner & Degreaser

DISTRIBUTOR / RETAILER			
Clements	Lowes	Benny's	Ames Discount Stores
Genuardis	Winn Dixie	Albertsons	C&S Wholesale
Wegmans	Food Mart	Stop N Shop	Spags
Food Lion	Edwards	Big Y	Nash Finch
MDI	Price Chopper	BJ Wholesale Club	Waldbaums
Ingles	Topps	Big V-Shoprite	

Table 5.2 Mail Order Suppliers of Citra-Solv® Natural Citrus Cleaner & Degreaser

COMPANY	ADDRESS	PHONE
The Vermont Country Store	PO Box 1108 Manchester, VT 05255	(802) 632 2400
Home Trends	1450 Lyell Avenue Rochester, NY 14606	(716) 254-6520
Walnut Acres	Penns Creek Road Penns Creek, PA 17862	(800) 433-3998
Environmentally Sound Products	167 Main Street Eldred, PA 16731	(800) 886-5432
Harmony	360 Interlocken Boulevard Suite 300 Broomfield, CO 80021	(800) 456-1177
Real Goods	966 Mazzoni Road Ukiah, CA 95482	(800) 762-7325
Solutions	13700 NW Science Park Dr. Portland, OR 97229	(800) 547-1160
Down To Earth	345 Lincoln Street Alley Eugene, OR 97401	(800) 234-5932
The Added Touch	132 Trafalgar Road Oakville, Ontario L6J 3G5	(800) 268-5060

In addition to Citra-Solv® Natural Citrus Cleaner & Degreaser, Shadow Lake®, Inc. also markets other products including oil-based air fresheners derived from natural ingredients such as citrus or vanilla and a natural all-purpose castile soap made primarily from olive, coconut, and other essential oils.

Contact Information:

Main Office and Plant Facility:

Shadow Lake®, Incorporated
Mr. Mike Riordan
188 Shadow Lake Road
Ridgefield, CT 06877-1032

Phone: (203) 778-0881
(800) 343-6588

E-mail: **shdwlake@ix.netcom.com**
Internet: **http://www.shadowlake.com/**

5.2 Vendor Claims and Specifications

Shadow Lake®, Inc. claims that d-limonene, the major ingredient in Citra-Solv®, is one of the most powerful solvents known to man. The manufacturer also claims that Citra-Solv® is so powerful that it can replace many harsh chemical cleaners including petroleum distillate products resulting in fewer toxic products in the workplace. In addition, the manufacturer claims that Citra-Solv® is biodegradable and environmentally friendly. The following list includes many of the manufacturer's claims regarding this product.

- Natural solvent made from the rinds of oranges
- Contains no petroleum distillates
- Biodegradable
- Extremely low toxicity even at high concentrations
- Super-concentrated multi-purpose cleaner (contains no water but is water soluble)
- Reduces waste

Tables 5.3a and 5.3b list many industrial, household, and automotive applications and the recommended dilution for Citra-Solv® Natural Citrus Cleaner and Degreaser. Table 5.4 lists the physical properties of Citra-Solv®.

Table 5.3a Industrial Cleaner/Solvent Applications for Citra-Solv® Natural Citrus Cleaner & Degreaser

CLEANING DILUTION	TYPES OF CLEANING APPLICATIONS	HOW TO USE CITRA-SOLV® DILUTION
Industrial Cleaner/Solvent		
10 oz full strength daily	Grease traps and drain lines	Add Citra-Solv, wait 1 hour and rinse with hot water
32 oz per 30 gallons of holding tank capacity	Clean and deodorize chemical toilets	Add measured amount of Citra-Solv to holding tank
1 qt per 1000 gal capacity	Sewage tanks, septic tanks, drain fields	Dispense through drip device for maximum odor control
1 oz per 16 oz water or up to full strength	Dip tanks, remove cutting oils, lubricants, varnishes and carbon deposits from machine parts	Add dilution to dip tank (up to full strength)
1 oz per 32 oz water (or up to 1:100 depending on pressure)	Pressure washing	For heavily soiled areas, apply full strength and let soak
1 oz per 8 oz water	Grease Filters	Place filter in sink or basin, spray on and let stand for 10 minutes
1 oz per 16 oz water	Smoke, soot and diesel fuel	Apply solution with sprayer or bristle brush to remove stains from firebrick, stone walls, etc.

Table 5.3b Household and Automotive Applications for Citra-Solv® Natural Citrus Cleaner & Degreaser

CLEANING DILUTION	TYPES OF CLEANING APPLICATIONS	HOW TO USE CITRA-SOLV® DILUTION
Household and Automotive Use		
Window & Glass Cleaner 1 oz in 3 gal water (384:1)	All glass surfaces, windows, windshield washer reservoirs	Apply pre-mixed dilution to soiled area, rinse with clean water, and wipe, buff, allow to air dry
General Purpose Cleaner 1 oz in 1/5 gal water (64:1)	Chrome, crystal, cars, trucks, motor homes, boats, bicycles, carpet cleaning machines, no-wax floors	
All-Purpose Cleaner 1 oz in 2 cups water (16:1)	Vents, sports equipment, walls, wall coverings, appliances, counters, vinyl, porcelain, wood, paneling, aluminum, stainless steel, metal blinds, telephones	
	Pre-spotting and spotting fabrics, carpet, upholstery, and fiber materials	Apply dilution to spots or soiled area, allow to stand for 1 minute brush and blot with damp cloth until stain is gone, lightly rinse with clean water, blot dry
Degreaser / Cleaner 1 oz in 1 cup water (8:1)	Vinyl car tops, fiberglass, concrete, fireplace surfaces, outdoor furniture, upholstery, oven ranges, food grease build up	Apply cleaner to soiled area by any standard method, allow to stand for a short period. Rinse with clean water, and dry with normal method. (wipe, buff, or allow to air dry)
Bathroom Cleaner 1 oz in ½ cup water (4:1)	Tub & tile, shower curtains, soap scum, machinery, tires, wheels, pet stains, & odors, petroleum stains	
Solvent / Spotter Full strength	Ovens, grills, engines, greasy parts, tar, grease, chewing gum, blood, fresh paints, crayons, waxes (paraffin), adhesives, permanent marker	

Table 5.4: Physical Properties of Citra-Solv® Natural Cleaner and Degreaser

PHYSICAL PROPERTIES	VALUE
Appearance	Orange liquid
Odor	Strong orange odor
Specific Gravity	0.859 ± 0.001
Boiling Point (°F)	310-330
Flash Point (°F) (Cleveland Open Cup)	142
Vapor Pressure (mm Hg)	2
Vapor Density	0.01
Solubility in Water	Miscible
% Volatile by Volume	90
Evaporation Rate	>1
pH	7.0-9.0

5.3 Verification of Product Claims

5.3.1 Third Party Testing and Results

5.3.1.1 SGS U.S. Testing Company, Incorporated

In December 1997, SGS U.S. Testing Company performed a 28 Day Shake Flask Ready Biodegradability Test on Citra-Solv® Cleaner and Degreaser to determine the test substance's biodegradability in a closed aqueous system. The test was conducted in a Gledhill Apparatus (Shake Flask) in compliance with U.S. EPA Good Laboratory Practice Standards, as described in 40 CFR, Part 792. Test results indicate that Citra-Solv® degraded 75.6% as determined by Total Organic Carbon (TOC) reduction and 209% by CO_2 evolution within 28 days. According to the test procedures used, Citra-Solv® met the criteria for "ready biodegradability".

A copy of the SGS test report titled *"28 Day Shake Flask Ready Biodegradability Test Versus Citra-Solv®"* is included in Appendix B.

5.3.1.2 National Institute of Environmental Health Services Toxicology and Carcinogenesis Studies of d-Limonene (CAS No. 5989-27-5)

Under the National Toxicology Program, the National Institute of Environmental Health Sciences conducted two-year toxicology and carcinogenesis studies of d-limonene, a naturally occurring monoterpene found in many volatile oils, especially in citrus oils. These tests were conducted because of widespread use of d-limonene as a flavor and fragrance additive for food and household cleaning products and its increasing use as an industrial solvent.

Under the conditions of the two-year studies, the National Institute of Environmental Health Sciences concluded that there was clear evidence of carcinogenic activity of d-limonene in male rats, as shown by increased incidences of tubular cell hyperplasia, adenomas, and adenocarcinomas of the kidney. The Institute concluded there was no evidence of carcinogenic activity of d-limonene in female rats that received 300 or 600 mg/kg, nor was there evidence of carcinogenic activity in male mice that received 250 or 500 mg/kg or female mice that received 500 or 1000 mg/kg. Most importantly, the Institute determined that the kidney cancer produced in male rats by d-limonene was caused by a biological process *unique* to male rats. Several other chemicals and substances, such as unleaded gasoline, produce kidney tumors in male rats by this same mechanism, which does not occur in other rodents or in humans.

A copy of the National Institute of Environmental Health Sciences report TR-347, *"Toxicology and Carcinogenesis Studies of d-Limonene (CAS No. 5989-27-5) in F344/N Rats and B6C3F$_1$ Mice (Gavage Studies)"*, is included in Appendix C. This, as well as additional information regarding d-limonene, is also available at the following web sites:

http://ntp-server.niehs.nih.gov/htdocs/LT-Studies/TR347.html
http://ntp-server.niehs.nih.gov/htdocs/Results_status/ResstatL/10071-T.html
It should also be noted that d-limonene is not listed in the Chemical Abstracts Service (CAS) Registry Number (CASRN) index which lists the chemical names and registry numbers for all entries in the National Toxicology Program's Eighth Report on Carcinogens. The Report on

Carcinogens discusses individual substances, mixtures of chemicals, or exposure circumstances associated with technological processes that are known to be human carcinogens or which may reasonably be anticipated to be human carcinogens. The report also contains information received from other Federal agencies relating to estimated exposures and exposure standards or guidelines. The National Toxicology Program's Eighth Report on Carcinogens and CASRN index can be found at the following web sites:

http://ntp-server.niehs.nih.gov/Main_pages/NTP_8RoC_pg.html
http://ntp-server.niehs.nih.gov/htdocs/8_RoC/CAS_AppG.html

5.3.1.3 Green Seal

Green Seal has recognized Citra-Solv® Natural Citrus Cleaner & Degreaser as being an environmentally responsible cleaner. Citra-Solv® received honorable mentions for recommended general purpose cleaners in the March 1998 issue of Green Seal's "*Choose Green Report*" featuring general purpose cleaners. The March 1998 issue of the "*Choose Green Report*" is included in Appendix D. Green Seal is an independent, nonprofit organization dedicated to protecting the environment by promoting the manufacture and sale of environmentally responsible consumer products. Green Seal's mission is to achieve significant environmental benefit by encouraging organizations and individuals to choose environmentally responsible products and services. This goal is accomplished in two ways. First, they set rigorous environmental standards for products and services and award a seal of approval to those that meet the standard. When consumers select products bearing the Green Seal, they know they are buying products that have a lessened impact on the environment, without sacrificing performance. Second, through the Green Seal Environmental Partners Program and the Choose Green Reports, they help large and small institutions become environmentally sensitive shoppers. Green Seal also provides detailed guidance on how organizations can protect the environment while saving money.

Contact Information:

GREEN SEAL
1400 Sixteenth Street, NW
Suite 300
Washington, DC 20036-2215
(202) 588-8400
(202) 588-8465 - FAX

http://www.greenseal.org/index.htm (Green Seal Home Page)
http://www.greenseal.org/chart.htm (Recommended General-Purpose Cleaners)
http://www.greenseal.org/standard/h-cleanr.htm (Environmental Standards for Household Cleaners)

To be recognized by Green Seal requires more than having the words "biodegradable" or "non-toxic" printed on the product label. Products must also meet the environmental criteria listed below:

- Product is non-toxic to aquatic life and humans. *Green Seal requires that cleaning products pass specific aquatic toxicity tests, which are listed in the Green Seal environmental*

standards for household cleaners. A copy of this standard (GS-08) is included in Appendix E.

- Product is biodegradable.
- Phosphate and phosphonate concentrations are less than 0.5% by weight.
- Product works optimally when diluted with cold water.
- Product is packaged as a concentrate in recyclable/refillable containers with post-consumer recycled content.

Additionally, products must perform not only to maintain consumer faith in green products but also help the environment. Less efficient cleaners that require excessive amounts of product to clean surfaces are not considered beneficial to the environment and would not be recognized favorably by Green Seal. Green cleaners identified in Table 5.5 meet these environmental criteria.

Green Seal is a nonprofit, environmental-labeling organization and views themselves as an environmental version of "Consumer Reports". Their goal is to develop stringent environmental standards for various products and serve to certify products that meet these standards. A "Green Seal of Approval" is awarded to products that meet stringent environmental standards, that cause less harm to the environment than other similar products, and have been certified by Green Seal.

Green Seal also publishes a monthly "Choose Green Report". This report consists of a comprehensive look at environmentally responsible "green" products with a comparative list of manufacturers and sources. Products that have been awarded the "Green Seal of Approval" are identified with the seal in the "certified" column. Green products, such as Citra-Solv® Natural Citrus Cleaner & Degreaser, which meet the Green Seal environmental standard for household cleaners, but have not been tested by Green Seal, are also included. These products do not possess the seal of approval but are nevertheless considered environmentally responsible or "green".

(Table 5.5 Omitted Due To Restricted Vendor Information)

5.3.1.4 Citra-Solv® Natural Citrus Cleaner & Degreaser Third Party Product/Performance Testing

Shadow Lake®, Inc. has not performed independent third party testing to validate product performance of Citra-Solv® Natural Citrus Cleaner & Degreaser. Vendor claims of product performance are based on case studies provided by Shadow Lake's supplier of the main ingredient (d-limonene) used in Citra-Solv®. Materials compatibility is a key issue with any solvent or cleaner to be used with equipment such as parts washers, dip tanks and pressure washers. The supplier has compiled a d-limonene compatibility chart as shown in Table 5.6.

Table 5.6: D-Limonene Compatibility Chart

D-LIMONENE COMPATIBILITY CHART	
Material	**Compatibility**
Aluminum	Very Good
Carbon/Ceramic	Very Good
Carbon/Graphite	Very Good
Carpenter 20	Very Good
Cast Bronze	Very Good
Ceramagnet A	Very Good
Ceramic	Very Good
CPVC	Very Good
Epoxy	Very Good
Kel-F (Reg TM E.I. du Pont de Nemous & Co.)	Very Good
Kynar (PVDF)(Reg TM Pennwalt Co.)	Very Good
Nylon	Very Good
Phenolic	Very Good
Ryton to 200°F (Reg TM Phillips Petroleum Co)	Very Good
Stainless Steel (304)	Very Good
Stainless Steel (316)	Very Good
Stainless Steel (440)	Very Good
Teflon (Reg TM E.I. du Pont de Nemous & Co.)	Very Good
Titanium	Very Good
Hastalloy	Very Good
Viton (Reg TM E.I. du Pont de Nemous & Co.)	Very Good
Buna N	Fair
Cycolac (ABS)(Reg TM Borg-Warner Co.)	Fair
PVC	Fair
Polyethylene	Not Recommended
Polypropylene	Not Recommended
Natural Rubber	Not Recommended
Neoprene	Not Recommended
Nitrll	Not Recommended
Tygon (Reg TM 3M Co.)	Not Recommended

The supplier also recommends that one should avoid contacting d-limonene with materials that can rust. Where rust may be a concern, Shadow Lake®, Inc., can increase the concentration of orange oil, a rust inhibitor, in the Citra-Solv® formula.
In addition to the above material compatibility information, case studies provided by the supplier give insight into the performance of d-limonene based cleaners such as Citra-Solv®. Several case studies involving d-limonene-based cleaners are presented in the following sections. These case studies demonstrate that d-limonene based cleaners such as Citra-Solv® have been successfully used to replace cleaners such as 1,1,1-trichloroethane (TCA), methyl ethyl ketone (MEK), methanol, and chlorofluorocarbons (CFC) in various industrial applications. Several of the case studies indicate significant savings in operating expenses and reduced hazardous waste disposal costs. In addition, d-limonene based cleaners such as Citra-Solv® provide a safer work environment for employees through reduced exposure to hazardous chemicals.

5.3.1.4.1 Case 1: Martin Marietta Astronautics

Martin Marietta Astronautics has replaced TCA and MEK with a terpene cleaner for hand wiping operations. The terpene cleaner was decided upon after 16 months of extensive testing of citrus and alkaline-based compounds. Workers prefer the citrus-based cleaner because it is more efficient. The terpene cleaner leaves less residue resulting in higher coating bond strength. Martin Marietta estimates the change has reduced toxic emissions by thousands of pounds per year. Research costs were $350,000 to find a suitable replacement for TCA and MEK. Estimated savings are $250,000 per year.

Dykema, Kevin J., and George R. Larson, 1993. "*Shifting the Environmental Paradigm at Martin Marietta Astronautics*", Pollution Prevention Review, Spring: 205.

5.3.1.4.2 Case 2: EPA and APS Materials, Incorporated

In a joint research effort, the U.S. EPA and APS Materials, Inc. have investigated the use of a limonene cleaner to replace TCA and methanol. APS Materials, Inc. is a metal finishing company that applies plasma coating to parts for use in hostile environments. In the biomedical parts division, cobalt, molybdenum and titanium parts are coated with a porous titanium layer for use as orthopedic implants. APS Materials has converted to the terpene cleaner as a result of the investigation. Cleaning efficacy is excellent with a slight increase in bonding strength for the limonene-cleaned parts. Changing to the aqueous system required the addition of rinse and dry stations. The new system cost $1,800 to install with annual operating expenses of $850. Net savings are $4,800 per year.

Brown, Lisa M., Johnny Springer, and Matthew Bower, 1992. "*Chemical Substitution for 1,1,1-Trichloroethane and Methanol in an Industrial Cleaning Operation*", Journal of Hazardous Materials, 29:179-188, Elsevier Science Publishers.

5.3.1.4.3 Case 3: GE Medical Systems of Waukesha, WI

GE Medical Systems of Waukesha, Wisconsin, is a manufacturer of medical diagnostic equipment. Spray cleaning (degreasing) of parts using TCA resulted in fugitive air emissions. GE Medical Systems eliminated the fugitive TCA emissions by changing to a terpene cleaner for degreasing. Degreasing with TCA required the purchase of 800 gallons of solvent per year, all of which was lost to the atmosphere. The terpene cleaner is much less volatile, requiring the purchase of only 30 gallons per year. The terpene cleaner is recycled. There was no capital expenditure required to implement the change in cleaning solution.

Wisconsin Department of Natural Resources, Case Study: GE Medical Systems*; "Replacing 1,1,1-tricholroethane with Citrus-Based Solvents*", PUBL-SW-168 92, Hazardous Waste Minimization Program (SW/3). Madison, WI.

5.3.1.4.4 Case 4: Northern Precision Casting of Lake Geneva, WI

Northern Precision Casting of Lake Geneva, Wisconsin, switched to a citrus-based solvent for cleaning the wax patterns used in making molds. Previously, they used TCA, which evaporated as fugitive emissions. TCA fugitive emissions amounted to 18,000 pounds in 1988. The terpene solvent is water-soluble and is discharged to a publicly owned treatment works. No capital costs were incurred for the change. Maintenance and operating costs are approximately the same.

Wisconsin Department of Natural Resources, Case Study: Northern Precision Casting; *"Replacing 1,1,1-Trichloroethane (TCA) with Citrus-Based Solvents*", PUBL-SW-161 92, Hazardous Waste Minimization Program (SW/3). Madison, WI.

5.3.1.4.5 Case 5: Marine Corps Air Station Naval Aviation Depot, Cherry Point, NC

The Marine Corps Air Station Naval Aviation Depot, Cherry Point, NC, is responsible for the complete maintenance/rebuilding of naval aircraft. In 1990 the depot used 8,000 gallons of CFC-113 and 15,600 gallons of 1,1,1-trichloroethane. By the end of 1992, CFC-113 usage had been reduced to 500 gallons annually, and TCA usage had been cut to approximately 4,800 gallons. The replacements included: soap bubbles for leak checks, aqueous power washers for electronics, motor, and engine shop use; terpene cleaners for hand wiping; steam cleaning or wet sodium bicarbonate blasting for soil and carbon removal; and plastic media blasting for paint removal.

Hazardous Minimization-Saving Time, Money, and the Environment, Fennell, Mary Beth and Roberts, James Mark/Naval Aviation Depot, Proceeding of the Aerospace Symposium, January 1993, Lake Buena Vista, Florida, pp. 39-46.

5.3.1.4.6 Case 6: AT&T Reduces CFC-113 Usage

AT&T has reduced its usage of CFC-113 by switching to a semi-aqueous chemistry for cleaning surface mount assemblies. Parts are fed by conveyor into a power washer consisting of wash and rinse/dry modules. Low and high-pressure sprays of a terpene cleaner are followed by nitrogen knives which reduce cleaning solution loss and blanket the washer with an inert atmosphere. In the second module, the parts are rinsed with low, then high-pressure water sprays to remove the terpene cleaner. Rinsing is followed by water removal by air knives within the same module. Care must be taken in selecting surface mount components because the terpene cleaner swells some plastic and elastomers. AT&T has found that the new cleaning method is more economical than the previous CFC-113 method.

"*Terpene Cleaning of Surface Mount Assemblies, Aqueous and Semi-Aqueous Alternatives for CFC-113 and Methyl Chloroform Cleaning of Printed Circuit Board Assemblies*", EPA/400/1-91/016, June 1991, pp. 51-60.

5.3.1.4.7 Case 7: Motorola Corporation Active Flux Removal Cleaning Systems

In 1998 the Motorola Corporation had 29 active flux removal cleaning systems using 250,000 pounds of CFC-113 annually. By August 1991, Motorola had eliminated CFC-113 usage. Many of their printed circuit board assemblies are now made with a no-clean flux. Assemblies which require cleaning are now cleaned using terpenes and water. Benefits reported include cleaner assemblies, less production downtime, and decreased cleaning cost. Cleaning costs are now about $8/hr with the terpene/water versus $38/hr for the CFC-113.

"*Terpene Cleaning of Printed Circuit Board Assemblies, Aqueous and Semi-Aqueous Alternatives for CFC-113 and Methyl Chloroform Cleaning of Printed Circuit Board Assemblies*", EPA/400/1-91/016, June 1991, pp. 61-62.

5.3.1.4.8 Case 8: Crown Equipment Corporation, New Bremen, OH

Crown Equipment Corporation, New Bremen, OH, manufactures electric lift and television antennae rotors. Mild steel, aluminum, cast iron, and copper are all used and cleaned at the plant. In 1988 Crown used 208,000 pounds of TCA in cold cleaning (dipping) and vapor degreasing operations. Hand dipping now uses a water-based cleaner with rust inhibitor added for corrosion resistance. 100% d-limonene spray cleaner has replaced TCA for hand wiped parts. An alkaline aqueous immersion cleaner has replaced one degreaser (with inhibitor added for ferrous parts). The other degreaser was replaced with an aqueous power washer which uses heat, agitation, and forced air drying to produce clean parts. The payback period for the capital expenses was 10 months. In 1989 Crown saved $100,000 in chemical costs. Crown Equipment has switched to water-based cleaning with no decrease in production. Employees prefer the water-based cleaner for hand dipping.

Case Studies: "*Multi-Industry Success Stories to Reduce TCA Use in Ohio"* Kohler, Kurt, and Anthony Sasson, Pollution Prevention Review, Autumn 1993, pp. 407-409.

5.3.1.4.9 Case 9: Bureau of Engraving, Inc., Industrial Division

The Bureau of Engraving, Industrial Division, manufactures printed circuit boards. In 1990 the company decided to eliminate the use of methylene chloride and TCA, which were being used at the rate of 681,000 pounds per year. Several changes in the manufacturing process were necessary to accomplish this goal, including the use of water-based and terpene-based cleaners. The Bureau of Engraving, Industrial Division, is saving $250,000 annually in purchase cost and another $20,000 in maintenance, energy, and disposal costs.

William T. Currie, Vice President, Facilities and Environmental Affairs, Bureau of Engraving, Inc., Industrial Division, 500 Fourth Street, Minneapolis, MN, 55415, MNTAP, 1993 Governor's Awards for Excellence in Pollution Prevention.

5.3.2 Review of Material Safety Data Sheet

The material safety data sheet for Citra-Solv® Natural Citrus Cleaner & Degreaser was prepared internally by Shadow Lake®, Inc. This product is formulated from 80-95 wt% d-limonene (CAS 5989-27-5), 1-10% folded orange oil (CAS 8028-48-6), 1-10% ethoxylated alcohols C9-C11 (CAS 68439-46-3), and 1-10 wt% coconut diethanolamide (CAS 61790-63-4) and has been shown to be readily biodegradable. The product is not considered to be a carcinogen by the National Toxicology Program (NTP), the International Agency for Research on Cancer (IARC), or the Occupational Safety and Health Administration (OSHA). Citra-Solv® does not contain, as an ingredient, chlorine, phenols, nitrites, heavy metals, arsenic, PCB, PCT, TCCD, or other dioxin related substances. Citra-Solv® Natural Citrus Cleaner & Degreaser may be harmful by inhalation, ingestion, skin absorption. Vapor or mist is irritating to the eyes, mucous membranes and upper respiratory tract. Certain individuals may develop contact dermatitis after exposure. A copy of the MSDS is included in Appendix F.

5.4 Military Specifications

Military specification MIL-C-29602 establishes the requirements for cleaning compounds used in power washers and spray cabinets for cleaning aircraft components. This document states that the flashpoint of the undiluted cleaning compound shall be greater than 212 ^{0}F. Since that flashpoint of Citra-Solv® was determined at 142 ^{0}F, Citra-Solv® would not meet the requirements of MIL-C-29602.

Military specification MIL-DTL-24800 establishes the cleaning compound to be used in immersion, ultrasonic, spray, and pumped cleaning of oxygen system piping and components. This document specifies that an aqueous inorganic cleaning compound shall be used for the above cleaning operations. Since Citra-Solv® is based on an organic material, it would not meet the requirements of MIL-DTL-24800.

Military specifications A-A-50425 and A-A-50427 establish the requirements for cleaning compounds used to clean oxygen system components and oxygen systems. Historically, TCA, CFC-113, 1,1-dichloro-1-fluoroethane, and HCFC-141B have been used to clean these items. The specification calls for a colorless, non-flammable cleaning compound. Although Citra-Solv® in its diluted form would be non-flammable, however it is not a colorless fluid and, therefore, would not meet the requirements of

A-A-50425 and A-A-50427.

5.5 Current Users

Citra-Solv® Natural Citrus Cleaner & Degreaser has been in production for nearly 10 years. This product is available from various distributors, retailers and mail order suppliers (Tables 5.1 and 5.2) to a wide variety of consumers. Table 5.7 is a list of major industrial users.

Table 5.7: Citra-Solv® Major Industrial Users

INDUSTRIAL USER	INDUSTRIAL USE
Char-Broil®	Citra-Solv® used as degreaser and parts cleaner in their manufacturing process
Coca-Cola®	Citra-Solv® used to remove adhesive over-sprays from two-liter bottling line. Also helps reduce the quantity of hazardous chemicals in bottling plant thereby keeping facility in compliance with government regulations.
Fisher Price®	Citra-Solv® used to clean plastic residue from toy molds in the manufacturing process.
Ford Motor Company	Citra-Solv® used in the Transmission Division in Livonia, MI.
Vibratech	Citra-Solv® used as a degreaser and parts cleaner in the manufacturing of automotive parts.
Wentworth Laboratories	Citra-Solv® used to remove excess soldering flux from assembled circuit boards during manufacturing process.

5.6 Product Comparisons

(Section 5.6 Omitted Due To Restricted Vendor Information)

5.7 Preliminary Life Cycle Costs

(Section 5.7 Omitted Due To Restricted Vendor Information)

5.8 Potential Navy / DoD Users

5.8.1 Federal Supply Listings

The Federal Government buys, stocks, and uses over 7 million items. The supply system catalog assigns National Stock Numbers (NSNs) to each item the Government uses. The NSN is a 13-digit number assigned by the Defense Logistics Service Center (DLSC), Battle Creek, Michigan. The first four digits identify the Federal Supply Class (FSC) of the product. The next nine numbers represent the National Item Identification Number (NIIN). The first two numbers of the NIIN identifies the country of origin. The remaining seven digits identifies the specific item. A summary and detailed FSC listing can be found at the following web site:

http://www.compnet.com/fsc.html (FSC listing)

The FSC system is most important in connection with DoD acquisitions of supplies and equipment. The identification is either by two-digit groups or by four-digit individual codes. Sometimes only the two-digit code is used which means that, in general; the same major buying offices buy most of the products in the group. In other cases, some or all of the four-digit codes are listed which means that there are differences in buying patterns.

Although Citra-Solv® Natural Citrus Cleaner & Degreaser has not been assigned a NSN, FSC codes identified in the Federal Supply System that could potentially include this product are 7910-7930. This range of code numbers is defined as "Cleaning Equipment & Supplies". Based on similar products currently available through the Federal Supply System, the most appropriate FSC code for Citra-Solv® is 7930. This code is defined as "Cleaning/Polishing Compounds and Preparations".

5.8.2 Potential Military Specific Uses for Citra-Solv®

The military uses a variety of cleaners, solvents and degreasers for maintenance and repair work. Citra-Solv has not been assigned a NSN and is currently not available through the Federal Supply System. Table 5.11 lists historical purchase data information for FSC Code 7930. This information is available at **http://www.acq.osd.mil/sadbu** under "Links" to estimate the potential market for products and services within DoD.

Table 5.11: FY97 Purchase Data for FSC Code 7930, "Cleaning/Polishing Compounds and Preparations" Contract Awards by FSC/SVC and Purchasing Office (in Thousands of Dollars)

Dept	State	City	Purchase Office	Total Acts.	Total Dollars	US Bus. Acts.	US Bus. Dollars	Small Bus. Acts.	Small Bus. Dollars
Army	KY	Fort Campbell	Directorate of Contracting	1	46	0	0	0	0
Army	CA	San Francisco	HQ, EUSA, ASST COFS ACQ. MGT.	1	68	0	0	0	0
Army	MD	Aberdeen Proving Ground	USA Aberdeen Proving Ground	1	48	0	0	0	0
Navy	CA	San Diego NSC	Fleet & Industrial Supply Center	1	32	0	0	0	0
Navy	VA	Norfolk	Fleet & Industrial Supply Center	1	32	0	0	0	0
Navy	FL	Jacksonville	Fleet & Industrial Supply Center	1	57	0	0	0	0
Navy	MD	Patuxent River NAS	Naval Air Warfare Center, Aircra	1	100	1	100	0	0
Navy	NY	New York	Naval Regional Contracting Center	2	259	0	0	0	0
Air Force	CA	San Francisco	CONS/LGC Mgmt Anly & Spt Flgt	2	84	1	28	1	28
Air Force	OH	Wright Patterson AFB	ASC/PKWT	1	139-	0	0	0	0
Air Force	OK	Tinker AFB	Oklahoma City ALC/PKO	1	26	0	0	0	0
OCE	CA	Sacramento	USA Engineer Dist Sacramento	1	27	1	27	1	27
			FSC TOTAL	**14**	**639**	**3**	**155**	**2**	**55**

5.9 Conclusions

- Citra-Solv® is predominantly derived from a sustainable renewable resource.
- Citra-Solv® is biodegradable.
- Citra-Solv® is not considered to be a carcinogen by the NTP, the IARC, or OSHA. Citra-Solv® does not contain, as an ingredient, chlorine, phenols, nitrites, heavy metals, arsenic, PCB, PCT, TCCD, or other dioxin related substances. However, Citra-Solv® may cause eye, respiratory, or skin irritations.
- Since Citra-Solv® is composed of up to 95% terpenes, Citra-Solv® can present a severe fire hazard and, therefore, not suitable for use in open pressurized spray cleaning systems without blanketing the system with an inert atmosphere (i.e. nitrogen).
- Citra-Solv® appears to be compatible with metals and most plastics. However, contact with polyethylene or polypropylene parts should be avoided.
- The Citra-Solv® formula with the rust inhibitor (orange oil) is better suited for applications where rust is a concern.
- Based on case studies provided by Shadow Lake's supplier of d-limonene, it is felt that Citra-Solv® is at least as effective as other d-limonene based products and could be included under FSC 7930 with other all-purpose cleaners and degreasers.
- Citra-Solv® does not meet the military specifications MIL-C-29602, MIL-DTL-24800, CID A-A-50425, or CID A-A-50427 for use as a cleaning compound in power washers and spray cabinets for cleaning aircraft components or as a cleaner for oxygen equipment, components, or systems.
- In some cleaning operations, degreasers such as Citra-Solv® have been successfully used to replace solvents such as TCA, MEK, methanol, and CFC-113 in various industrial applications.

5.10 Recommendations

Based upon the case studies of material substitutions with very similar citrus-based cleaners, no additional testing on Citra-Solv® Natural Citrus Cleaner & Degreaser as a general all-purpose cleaner is considered necessary. However, Citra-Solv® does not meet military specifications MIL-C-29602, CID A-A-50425, or CID A-A-50427 and, therefore, Citra-Solv® shall not be used or promoted as a cleaning compound in power washers and spray cabinets for cleaning aircraft components or as a cleaner for oxygen equipment or systems.

5.11 Implementation

5.11.1 Points of Contact

The DoD is ready to do business, on a competitive basis, with competent firms that can supply the products or services it needs. Manufacturers and marketing groups must familiarize themselves by learning how the DoD conducts business, and by seeking out those military purchasing offices that buy the products and services they can supply.

The Internet provides a valuable tool for businesses to obtain information on selling their products to the military. A comprehensive 6-Part handbook titled "*Selling To The Military*" is maintained on the World Wide Web by the Office of the Secretary of Defense, in Washington, DC (http://www.acq.osd.mil/sadbu/publications/selling/). This handbook is intended to provide firms, which have little or no experience in selling to DoD, with basic information about how the DoD conducts its business, and with specific information for locating sales opportunities. Part 2 addresses products and services bought by major military purchasing offices and is divided into two sections. The first section lists the major military purchasing offices of the Army, Navy, Air Force, and Defense Logistics Agency (DLA). The accompanying description summarizes the procurement responsibilities of each of these offices. The second section of this part lists the products and services purchased by the major military purchasing offices. It is easier to locate sales opportunities for specific items from this list. These items are listed in the numerical sequence of their FSC codes. This document includes information regarding historical purchases of goods and services by various military organizations. The information identifies the purchasing office, includes number of procurement actions performed, and specifies the total dollars spent on acquiring products and services.

Part 6 of the handbook contains additional information on offices providing assistance to small businesses for defense procurement. The contract management commands can assist in identifying DoD contracting offices likely to buy specific products or services. In addition, several publications are available to assist businesses with defense procurement. These publications include:

"U.S. Government Purchasing and Sales Directory"

> This document provides a listing of products and services bought by all Federal agencies, and is keyed to the purchasing offices that buy them. The DoD Stock Number is 045-000-00272-1 and is available from the Superintendent of Documents, U.S. Government printing office, Washington, D.C. 20402.

"Small Business Specialists"

> On a nationwide basis, this document lists DoD specialists by name, location, and phone number, and is available from the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402. The DoD reference number is DoD 4205.1-H. These regulations can also be found on the Internet at: http://www.acq.osd.mil/sadbu, click on "Publications".

Table 5.12 lists the major buying offices or procuring agencies within the military that have a history of purchasing items identified by FSC Code 7930.

Table 5.12: Purchasing Offices for Items Identified by FSC Code

MILITARY AND GOVERNMENT PRUCHASING OFFICES	FSC
Directorate of Contracting 2174 13 ½ ST Fort Campbell KY 42223-5358 (502) 798-7126	7930
A-2 U. S. Army Chemical Biological Defense Command AMSCB-SBA(A) Aberdeen Proving Ground, MD 21010-5423 (410) 671-3136	7930
Fleet and Industrial Supply Center Code COA 937 N. Harbor Drive San Diego, CA 92132 -5075 (619) 532-3439	7930
Fleet and Industrial Supply Center Code 04, Bldg W-143, Suite 600 1968 Gilbert Street Norfolk, VA 23511-3392 (757) 443-1435	7930
Naval Air Warfare Center Aircraft Division, Code 20C00W 22347 Cedar Point Road, Unit 6 Patuxent River, MD 20670-1161 (301) 342-7567 Ext. 103	7930
Aeronautical Systems Center (ASC/BC) 2196 D Street Wright-Patterson AFB, OH 45433-7201 (937)255-5422	7930
Oklahoma City Air Logistics Center 3001 Staff Dr, Suite 1AJ84A Tinker AFB, OK 73145-3009 (405)739-2601	7930

One obstacle to the implementation of Citra-Solv® is that people tend to resist change. It is difficult to persuade consumers to try a new product when they feel comfortable with what they are currently using. Therefore, procuring agencies must actively advertise their desire to purchase non-toxic and environmentally safe products within their organizations. This goal can be attained through internal promotion. The process is a broad-based employee education program that will affirm the procurement policy of an agency through advertising, workshops, agency newsletters, and technical and staff manuals.

Section 6.0 contains detailed implementation methods and additional procurement contacts applicable to Shadow Lake®, Inc. products.

5.11.2 Additional Implementation Processes

Product visibility is crucial to product implementation. The following processes will assist Shadow Lake®, Inc. product visibility within the military:

- The Defense Technical Information Center (DTIC) will receive a final copy of this report. Joint-Service users can search for specific information using a "key words or phrases" search engine.
- Citra-Solv will be logged into the Joint Service Pollution Prevention Technical Library. This library exists as a Web site and is accessed by the Tri-Service system for pollution prevention guidance.